

Chapter 2

Biofuels

2.1 Introduction to Biofuels

Known petroleum reserves are limited and will eventually run out. Various studies put the date of the global peak in oil production between 1996 and 2035. Biomass energy technologies use waste or plant matter to produce energy with a lower level of greenhouse gas emissions than fossil fuel sources (Sheehan *et al.*, 1998). In developed countries there is a growing trend toward employing modern technologies and efficient bioenergy conversion using a range of biofuels, which are becoming cost competitive with fossil fuels (Puhan *et al.*, 2005). The biofuel economy will grow rapidly during the 21st century. The biofuel economy, and its associated biorefineries, will be shaped by many of the same forces that shaped the development of the hydrocarbon economy and its refineries over the past century. President Bush spoke in his January 31, 2006 State of the Union address of producing biofuels by 2012 using “woodchips, stalks, and switchgrass” as the source of cellulosic biomass. These represent both existing and potential biomass resources. Due to the environmental merits of biofuel, its share in the automotive fuel market will grow rapidly in the next decade.

Various scenarios have put forward estimates of biofuel from biomass sources in the future energy system. In the most biomass-intensive scenario, by 2050 modernized biomass energy will contribute about one half of the total energy demand in developing countries (IPCC, 1997). The biomass-intensive future energy supply scenario includes 385 million ha of biomass energy plantations globally in 2050, with three quarters of this area established in developing countries (Kartha and Larson, 2000). The availability of biofuel resources is important for the electricity, heat, and liquid fuel market. There are two global biomass-based liquid transportation fuels that might replace gasoline and diesel fuel. These are bioethanol and biodiesel. Transport is one of the main energy-consuming sectors. It is assumed that biodiesel will be used as a fossil diesel replacement and that bioethanol will be used as a gasoline replacement. Biomass-based energy sources for heat, electricity, and transportation fuels are potentially carbon dioxide neutral and recycle the same carbon atoms. Due to the widespread availability of biomass resources,

biomass-based fuel technology can potentially employ more people than fossil-fuel-based technology (Demirbas, 2006a). Demand for energy is increasing every day due to the rapid growth of population and urbanization. As the major conventional energy sources like coal, petroleum, and natural gas are gradually depleted, biomass is emerging as one of the promising environmentally friendly renewable energy options.

The term biofuel refers to liquid or gaseous fuels for the transport sector that are predominantly produced from biomass. It is generally held that biofuels offer many benefits, including sustainability, reduction of greenhouse gas emissions, and security of supply (Reijnders, 2006). A variety of fuels can be produced from biomass resources including liquid fuels, such as ethanol, methanol, biodiesel, and Fischer-Tropsch diesel, and gaseous fuels, such as hydrogen and methane. Biofuels are primarily used in vehicles but can also be used in engines or fuel cells for electricity generation.

There are several reasons why biofuels are considered relevant technologies by both developing and industrialized countries (Demirbas, 2006a). They include energy security, environmental concerns, foreign exchange savings, and socio-economic issues related to the rural sector. Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade (Kim and Dale, 2005; Demirbas and Balat, 2006). The advantages of biofuels are the following: (a) they are easily available from common biomass sources, (b) carbon dioxide cycle occurs in combustion, (c) they are very environmentally friendly, and (d) they are biodegradable and contribute to sustainability (Puppan, 2002).

Various scenarios have led to the conclusion that biofuels will be in widespread use in the future energy system. The scenarios are to facilitate the transition from the hydrocarbon economy to the carbohydrate economy by using biomass to produce bioethanol and biomethanol as replacements for traditional oil-based fuels and feedstocks. The biofuel scenario produces equivalent rates of growth in GDP and per-capita affluence, reduces fossil energy intensities of GDP, and reduces oil imports. Each scenario has advantages whether in terms of rates of growth in GDP, reductions in carbon dioxide emissions, the energy ratio of the production process, the direct creation of jobs, or the area of biomass plantation required to make the production system feasible (Demirbas, 2006a).

The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels have oxygen levels of 10 to 45% while petroleum has essentially none, making the chemical properties of biofuels very different from those of petroleum. All have very low sulfur levels and many have low nitrogen levels.

Biomass can be converted into liquid and gaseous fuels through thermochemical and biological methods. Biofuel is a non-polluting, locally available, accessible, sustainable, and reliable fuel obtained from renewable sources (Vasudevan *et al.*, 2005). Liquid biofuels fall into the following categories: (a) vegetable oils and biodiesels, (b) alcohols, and (c) biocrude and synthetic oils. Figure 2.1 shows the sources of the main liquid biofuels for automobiles.

Biomass is an attractive feedstock for three main reasons. First, it is a renewable resource that could be sustainably developed in the future. Second, it appears

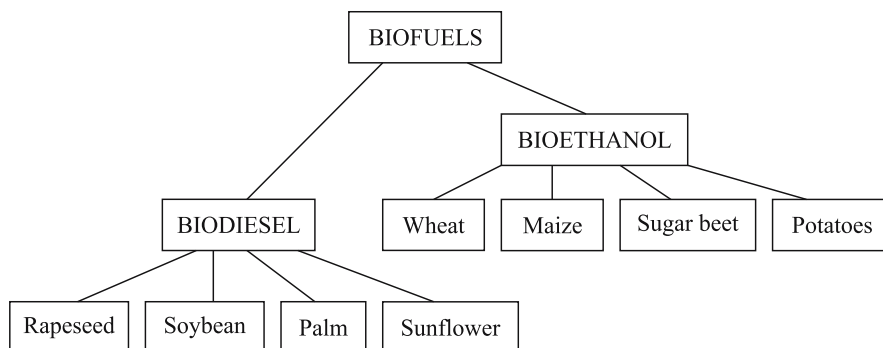


Fig. 2.1 Sources of main liquid biofuels for automobiles

to have formidably positive environmental properties resulting in no net releases of carbon dioxide and very low sulfur content. Third, it appears to have significant economic potential provided that fossil fuel prices increase in the future (Cadenas and Cabezudo, 1998). Lignocellulosic biomethanol has such low emissions because the carbon content of the alcohol is primarily derived from carbon that was sequestered in the growing of the biofeedstock and is only being rereleased into the atmosphere (Difiglio, 1997).

Carbohydrates (hemicelluloses and cellulose) in plant materials can be converted into sugars by hydrolysis. Fermentation is an anaerobic biological process in which sugars are converted into alcohol by the action of microorganisms, usually yeast. The resulting alcohol is bioethanol. The value of any particular type of biomass as feedstock for fermentation depends on the ease with which it can be converted into sugars. Bioethanol is a petrol additive/substitute. It is possible that wood, straw, and even household wastes may be economically converted into bioethanol. Ethanol demand is expected to more than double in the next ten years. For the supply to be available to meet this demand, new technologies must be moved from the laboratories to commercial reality (Bothast and Schlicher, 2005). World ethanol production is about 60% from sugar-crop feedstock.

Anaerobic digestion of biowastes occurs in the absence of air; the resulting gas, called biogas, is a mixture consisting mainly of methane and carbon dioxide. Biogas is a valuable fuel that is produced in digesters filled with feedstock like dung or sewage. The digestion is allowed to continue for a period of ten days to a few weeks (Demirbas, 2006b).

The Fischer–Tropsch synthesis (FTS) produces hydrocarbons of different lengths from a gas mixture of H_2 and CO (syngas) resulting from biomass gasification called bio-syngas. The fundamental reactions of synthesis gas chemistry are methanol synthesis, FTS, oxosynthesis (hydroformylation), and methane synthesis (Prins *et al.*, 2004). The FTS process is capable of producing liquid hydrocarbon fuels from bio-syngas. The large hydrocarbons can be hydrocracked to form mainly diesel of excellent quality. The process for producing liquid fuels from biomass, which integrates biomass gasification with FTS, converts a renewable

feedstock into a clean fuel. The products of FTS are mainly aliphatic straight-chain hydrocarbons (C_xH_y). Besides the C_xH_y , branched hydrocarbons, unsaturated hydrocarbons, and primary alcohols are also formed in minor quantities (Dry, 1999; Anderson, 1984; Bukur *et al.*, 1995; Schulz, 1999; Tijmensen *et al.*, 2002; May, 2003). The products obtained from FTS include the light hydrocarbons methane (CH_4), ethene (C_2H_4) and ethane (C_2H_6), LPG (C_3 – C_4 , propane and butane), gasoline (C_5 – C_{12}), diesel fuel (C_{13} – C_{22}), and waxes (C_{23} – C_{33}). The distribution of the products depends on the catalyst and the process parameters such as temperature, pressure, and residence time. The FTS has been extensively investigated by many researchers (Rapagna *et al.*, 1998; Sie *et al.*, 1999; Ahón *et al.*, 2005; Mirzaei *et al.*, 2006).

Vegetable oils from renewable oil seeds can be used when mixed with diesel fuels. Pure vegetable oil, however, cannot be used in direct-injection diesel engines, such as those regularly used in standard tractors, since engine cooking occurs after several hours of use. Conversion of vegetable oils and animal fats into biodiesel has been undergoing further development over the past several years (Prakas, 1998; Madras *et al.*, 2004; Haas *et al.*, 2006; Meher *et al.*, 2006). Biodiesel represents an alternative to petroleum-based diesel fuel. Chemically speaking, biodiesel is a mixture of monoalkyl esters of fatty acids, most often obtained from extracted plant oils and/or collected animal fats. Commonly accepted biodiesel raw materials include the oils from soy, canola, corn, rapeseed, and palm. New plant oils that are under consideration include mustard seed, peanut, sunflower, and cotton seed. The most commonly considered animal fats include those derived from poultry, beef, and pork (Usta *et al.*, 2005).

Ethanol is the most widely used liquid biofuel. It is an alcohol and is fermented from sugars, starches, or cellulosic biomass. Most commercial production of ethanol is from sugar cane or sugar beet, as starches and cellulosic biomass usually requires expensive pretreatment. Ethanol is used as a renewable energy fuel source as well as for the manufacture of cosmetics and pharmaceuticals and also for the production of alcoholic beverages. Ethyl alcohol is not only the oldest synthetic organic chemical used by humans, but it is also one of the most important. In an earlier study (Taherzadeh, 1999), the physiological effects of inhibitors on ethanol from lignocellulosic materials and fermentation strategies were comprehensively investigated.

2.2 Bioethanol

Carbohydrates (hemicelluloses and cellulose) in plant materials can be converted into sugars by hydrolysis. Fermentation is an anaerobic biological process in which sugars are converted into alcohol by the action of microorganisms, usually yeast. The resulting alcohol is ethanol. The value of any particular type of biomass as feedstock for fermentation depends on the ease with which it can be converted into sugars.

Table 2.1 Ethanol production on different continents (billion liters/year)

America	Asia	Europe	Africa	Oceania
22.3	5.7	4.6	0.5	0.2

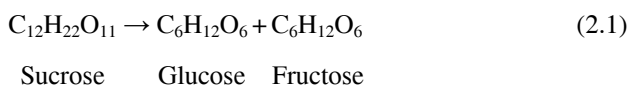
Cellulose is a remarkable pure organic polymer, consisting solely of units of anhydroglucose held together in a giant straight-chain molecule. Cellulose must be hydrolyzed into glucose before being fermented into ethanol. The conversion efficiencies of cellulose into glucose may depend on the extent to which chemical and mechanical pretreatments are able to structurally and chemically alter the pulp and paper mill wastes. The method of pulping, the type of wood, and the use of recycled pulp and paper products could also influence the accessibility of cellulose to cellulase enzymes (Adeeb, 2004).

Cellulose is insoluble in most solvents and has a low accessibility to acid and enzymatic hydrolysis. Hemicelluloses (arabinoglycuronoxylan and galactoglucomannans) are related to plant gums in composition and occur in much shorter molecule chains than cellulose. Hemicelluloses, which are present in deciduous woods chiefly as pentosans and in coniferous woods almost entirely as hexosanes, undergo thermal decomposition very readily. Hemicelluloses are derived mainly from chains of pentose sugars and act as the cement material holding together the cellulose micelles and fiber (Theander, 1985). Hemicelluloses are largely soluble in alkali and as such are more easily hydrolyzed.

Bioethanol is a fuel derived from renewable sources of feedstock, typically plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol is a petrol additive/substitute. Table 2.1 shows ethanol production on different continents.

Bioethanol can be used as a 5% blend with petrol under EU quality standard EN 228. This blend requires no engine modification and is covered by vehicle warranties. With engine modification, bioethanol can be used at higher levels, for example, E85 (85% bioethanol).

Bioethanol can be produced from a large variety of carbohydrates with a general formula of $(\text{CH}_2\text{O})_n$. Fermentation of sucrose is performed using commercial yeast such as *Saccharomyces cerevisiae*. The chemical reaction consists of enzymatic hydrolysis of sucrose followed by fermentation of simple sugars (Berg, 1988). First, invertase enzyme in the yeast catalyzes the hydrolysis of sucrose to convert it into glucose and fructose:



Second, zymase, another enzyme also present in yeast, converts the glucose and the fructose into ethanol:



Glucoamylase enzyme converts the starch into D-glucose. The enzymatic hydrolysis is then followed by fermentation, distillation, and dehydration to yield

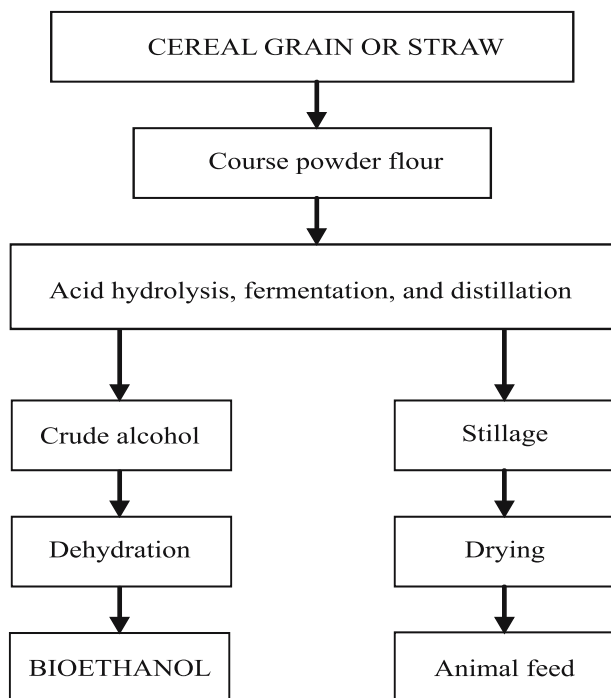


Fig. 2.2 Flow chart for the production of bioethanol from cereal grain or straw

anhydrous bioethanol. Corn (60 to 70% starch) is the dominant feedstock in the starch-to-bioethanol industry worldwide.

Carbohydrates (hemicelluloses and cellulose) in lignocellulosic materials can be converted into bioethanol. The lignocellulose is subjected to delignification, steam explosion, and dilute acid prehydrolysis, which is followed by enzymatic hydrolysis and fermentation into bioethanol (Baltz *et al.*, 1982; Castro *et al.*, 1993; Sokhansanj *et al.*, 2002; Kim and Dale, 2005). A major processing step in an ethanol plant is enzymatic saccharification of cellulose into sugars through treatment by enzymes; this step requires lengthy processing and normally follows a short-term pretreatment step (Kumar *et al.*, 2005). Figure 2.2 shows the flow chart for the production of bioethanol from cereal grain or straw.

Hydrolysis breaks down the hydrogen bonds in the hemicellulose and cellulose fractions into their sugar components: pentoses and hexoses. These sugars can then be fermented into bioethanol. The most commonly applied methods can be classified into two groups: chemical hydrolysis (dilute and concentrated acid hydrolysis) and enzymatic hydrolysis. In chemical hydrolysis, pretreatment and hydrolysis may be carried out in a single step. There are two basic types of acid used in hydrolysis: dilute acid and concentrated acid.

The biggest advantage of dilute acid processes is their fast rate of reaction, which facilitates continuous processing. Since 5-carbon sugars degrade more rap-

idly than 6-carbon sugars, one way to decrease sugar degradation is to have a two-stage process. The first stage is conducted under mild process conditions to recover the 5-carbon sugars, while the second stage is conducted under harsher conditions to recover the 6-carbon sugars.

Concentrated sulfuric or hydrochloric acid is used for the hydrolysis of lignocellulosic materials. The concentrated acid process uses relatively mild temperatures, and the only pressures involved are those created by pumping materials from vessel to vessel. Reaction times are typically much longer than for dilute acid. This process provides a complete and rapid conversion of cellulose into glucose and hemicelluloses into 5-carbon sugars with little degradation. The critical factors needed to make this process economically viable are to optimize sugar recovery and cost effectively recover the acid for recycling. The solid residue from the first stage is dewatered and soaked in a 30 to 40% concentration of sulfuric acid for 1 to 4 h as a precellulose hydrolysis step. The solution is again dewatered and dried, increasing the acid concentration to about 70%. After reacting in another vessel for 1 to 4 h at low temperatures, the contents are separated to recover the sugar and acid. The sugar/acid solution from the second stage is recycled to the first stage to provide the acid for first-stage hydrolysis (Demirbas, 2006b). The primary advantage of the concentrated acid process is the potential for high sugar recovery efficiency. The acid and sugar are separated via ion exchange, and then the acid is reconcentrated via multiple-effect evaporators.

2.3 Biomethanol

Methanol is one possible replacement for conventional motor fuels. It has been seen as a possible large-volume motor fuel substitute at various times during gasoline shortages. It was often used in the early part of the century to power automobiles before inexpensive gasoline was widely introduced. Synthetically produced methanol was widely used as a motor fuel in Germany during World War II. Methanol is commonly used in biodiesel production for its reactivity. The use of methanol as a motor fuel received attention during the oil crises of the 1970s due to its availability and low cost. Problems occurred early in the development of gasoline-methanol blends. As a result of its low price, some gasoline marketers overblended. Many tests have shown promising results using 85 to 100% by volume methanol as a transportation fuel in automobiles, trucks, and buses.

Methanol, also known as “wood alcohol”, is generally easier to find than ethanol. Sustainable methods of methanol production are currently not economically viable. Methanol is produced from synthetic gas or biogas and evaluated as a fuel for internal combustion engines. The production of methanol is a cost-intensive chemical process. Therefore, in current conditions, only waste biomass such as old wood or biowaste is used to produce methanol (Vasudevan *et al.*, 2005).

Methanol is poisonous and burns with an invisible flame. Like ethyl alcohol, it has a high octane rating, and hence an Otto engine is preferable. Most processes

require supplemental oxygen for the intermediate conversion of the biomass into a synthesis gas ($\text{H}_2 + \text{CO}$). A readily available supply of hydrogen and oxygen, therefore, should improve the overall productivity of biomass-derived methanol (Ouellette *et al.*, 1997).

Before modern production technologies were developed in the 1920s, methanol was obtained from wood as a coproduct of charcoal production and for this reason was commonly known as wood alcohol. Methanol is currently manufactured worldwide by conversion or derived from syngas, natural gas, refinery offgas, coal, or petroleum:



The chemical composition of syngas from coal and then from natural gas can be identical with the same H_2/CO ratio. A variety of catalysts are capable of causing the conversion, including reduced NiO-based preparations, reduced Cu/ZnO shift preparations, Cu/SiO₂ and Pd/SiO₂, and Pd/ZnO (Takezawa *et al.*, 1987; Iwasa *et al.*, 1993).

Methanol is currently made from natural gas but can also be made using biomass via partial oxidation reactions (Demirbas and Gullu, 1998). Biomass and coal can be considered potential fuels for gasification and further syngas production and methanol synthesis (Takezawa *et al.*, 1987). Adding sufficient hydrogen to the synthesis gas to convert all of the biomass into methanol carbon more than doubles the methanol produced from the same biomass base (Phillips *et al.*, 1990). Waste material can be partially converted into methanol, and the product yield for the conversion process is estimated to be 185 kg of methanol per metric ton of solid waste (Brown *et al.* 1952; Sorensen 1983). Agri-(m)ethanol is at present more expensive than synthesis ethanol from ethylene and methanol from natural gas (Grassi 1999).

Biomass resources can be used to produce methanol. The pyroligneous acid obtained from wood pyrolysis consists of about 50% methanol, acetone, phenols, and water (Demirbas and Gullu, 1998; Gullu and Demirbas, 2001). As a renewable resource, biomass represents a potentially inexhaustible supply of feedstock for methanol production. The composition of bio-syngas from biomass for producing methanol is presented in Table 2.2. Current natural gas feedstocks are so inexpensive that even with tax incentives renewable methanol has not been able to compete economically. Technologies are being developed that may eventually result in the commercial viability of renewable methanol.

Methanol from coal could be a very important source of liquid fuel in the future. The coal is first pulverized and cleaned, then fed to a gasifier bed, where it is reacted with oxygen and steam to produce syngas. Once these steps have been taken, the production process is much the same as with other feedstocks with some variations in the catalyst used and the design of the converter vessel in which the reaction is carried out. Methanol is made using synthesis gas (syngas) with hydrogen and carbon monoxide in a 2-to-1 ratio (Table 2.2). The syngas is transformed into methanol in a fixed-catalyst-bed reactor. Coal-derived methanol has many preferable properties: it is free of sulfur and other impurities, it could replace

Table 2.2 Composition of bio-syngas from biomass gasification

Constituents	% by volume (dry and nitrogen free)
Carbon monoxide (CO)	28–36
Hydrogen (H ₂)	22–32
Carbon dioxide (CO ₂)	21–30
Methane (CH ₄)	8–11
Ethene (C ₂ H ₄)	2–4

petroleum in transportation or be used as a peaking fuel in combustion turbines, or it could serve as a source of hydrogen for fuel cells. The technology for making methanol from natural gas is already in place and requires only efficiency improvements and scaling up to make methanol an economically viable alternative transportation fuel (Demirbas, 2000).

In recent years, a growing interest has been observed in the application of methanol as an alternative liquid fuel that can be used directly for powering Otto engines or fuel cells (Chmielniak and Sciazko, 2003). The feasibility of achieving the conversion has been demonstrated in a large-scale system in which a product gas is initially produced by pyrolysis and gasification of a carbonaceous matter. Syngas from biomass is altered by catalyst under high pressure and temperature to form methanol. This method will produce 100 gallons of methanol per ton of feed material (Rowell and Hokanson, 1979).

The gases produced can be steam reformed to produce hydrogen and followed by water-gas-shift reaction to further enhance hydrogen production. When the moisture content of biomass is higher than 35%, it can be gasified with supercritical water (Hao and Guo, 2002). Supercritical water gasification is a promising process to gasify biomass with high moisture content due to a high gasification ratio (100% achievable) and high hydrogen volumetric ratio (50% achievable) (Yoshida *et al.*, 2004; Matsumura and Minowa, 2004). Hydrogen produced by biomass gasification was reported to be comparable to that by natural gas reforming (Bowen *et al.*, 2003). The process is more advantageous than fossil fuel reforming due to the environmental benefits. It is expected that biomass thermochemical conversion will emerge as one of the most economical large-scale renewable hydrogen technologies.

The strategy is based on producing hydrogen from biomass pyrolysis using a coproduct strategy to reduce the cost of hydrogen and it was concluded that only this strategy could compete with the cost of commercial hydrocarbon-based technologies (Wang *et al.*, 1998). This strategy will demonstrate how hydrogen and biofuels are economically feasible and can foster the development of rural areas when practiced on a larger scale. The process of converting biomass into activated carbon is an alternative route to producing hydrogen with a valuable coproduct that is practiced commercially (Demirbas, 1999).

The simultaneous production of biomethanol (obtained by the hydrogenation of CO₂ developed during the fermentation of sugar juice), in parallel with the production of bioethanol, appears economically attractive in locations where hydro-

electricity is available at very low cost (~US\$0.01 per Kwh) and where lignocellulosic residues are available as surpluses.

The gas is converted into methanol in a conventional steam-reforming/water-gas-shift reaction followed by high-pressure catalytic methanol synthesis:



Eqs. (2.4) and (2.5) are called gasification/shift reactions.



or



Eqs. (2.6) and (2.7) are methanol synthesis reactions. Figure 2.3 shows production of biomethanol from carbohydrates by gasification and partial oxidation with O_2 and H_2O .

The energy value of residues generated worldwide in agriculture and the forest-products industry amounts to more than one third of the total commercial primary

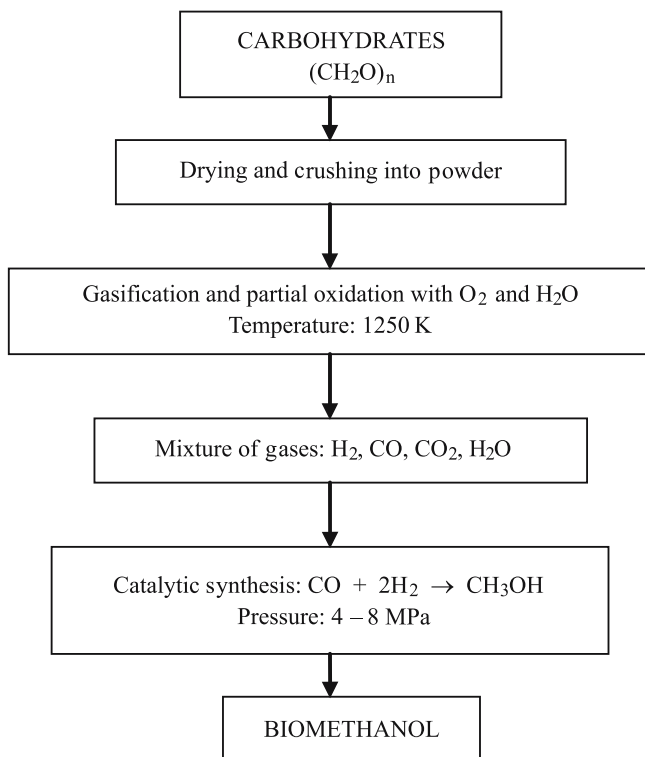


Fig. 2.3 Biomethanol from carbohydrates by gasification and partial oxidation with O_2 and H_2O

Table 2.3 Main production facilities of methanol and biomethanol

Methanol	Biomethanol
Catalytic synthesis from CO and H ₂	Catalytic synthesis from CO and H ₂
Natural gas	Distillation of liquid from wood pyrolysis
Petroleum gas	Gaseous products from biomass gasification
Distillation of liquid from coal pyrolysis	Synthetic gas from biomass and coal

energy use at present (Hall *et al.*, 1993). Bioenergy supplies can be divided into two broad categories: (a) organic municipal waste and residues from the food and materials sectors and (b) dedicated energy-crop plantations. Bioenergy from biomass, both residues and energy crops, can be converted into modern energy carriers such as hydrogen, methanol, ethanol, or electricity (Azar *et al.*, 2003).

Methanol can be produced from biomass. Thus the choice of fuel in the transportation sector is to some extent determined by the availability of biomass. As regards the difference between hydrogen and methanol production costs, the conversion of natural gas, biomass, and coal into hydrogen is generally more energy efficient and less expensive than conversion into methanol (Azar *et al.*, 2003). The main production facilities of methanol and biomethanol are given in Table 2.3.

2.4 Biohydrogen from Biomass by Steam Reforming

Biomass is a mixture of structural constituents (hemicelluloses, cellulose, and lignin) and minor amounts of extractives each of which pyrolyzes at different rates and by different mechanisms and pathways. All biomass materials can be converted into energy via thermochemical and biological processes. Of all the thermochemical conversion technologies, biomass gasification has attracted the most interest as it offers higher efficiencies in relation to combustion, whereas flash pyrolysis is still in the development stage (Demirbas and Arin, 2002). It is believed that as the reaction progresses the carbon becomes less reactive and forms stable chemical structures, and consequently the activation energy increases as the conversion level of biomass increases (Tran and Charanjit, 1978).

Biomass gasification can be considered as a form of pyrolysis, which takes place in higher temperatures and produces a mixture of gases with H₂ content ranging between 6 and 6.5% (McKendry, 2002; Bridgwater, 2003). Hydrogen can be produced from biomass via two thermochemical processes: (1) gasification followed by reforming of the syngas and (2) fast pyrolysis followed by reforming of the carbohydrate fraction of the bio-oil. In each process, water-gas shift is used to convert the reformed gas into hydrogen and pressure swing adsorption is used to purify the product.

Power generation from gaseous products from biomass gasification has been found to be the most promising biomass gasification technology. Gasification technologies provide the opportunity to convert renewable biomass feedstocks

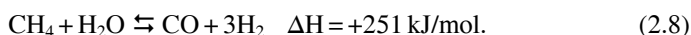
into clean fuel gases or synthesis gases. The synthesis gases include mainly hydrogen and carbon monoxide ($\text{H}_2 + \text{CO}$), which is also known as syngas. Bio-syngas is a gas rich in CO and H_2 obtained by gasification of biomass (Maschio *et al.*, 1994).

Currently, hydrogen is most economically produced from natural gas. The most studied technology for hydrogen production is steam-methane reforming, in which methane reacts with steam to produce a mixture of hydrogen, carbon dioxide, and carbon monoxide.

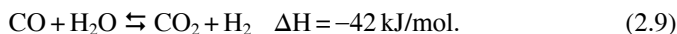
2.4.1 Steam-reforming Process

In the steam-reforming reaction, steam reacts with hydrocarbons in the feed to produce mainly carbon monoxide and hydrogen, commonly called synthesis gas. Steam reforming can be applied to various solid waste materials including municipal organic waste, waste oil, sewage sludge, paper mill sludge, black liquor, refuse-derived fuel, and agricultural waste. Steam reforming of natural gas, sometimes referred to as steam methane reforming, is the most common method of producing commercial bulk hydrogen. Steam reforming of natural gas is currently the least expensive method of producing hydrogen and is used for about half of the world's production of hydrogen.

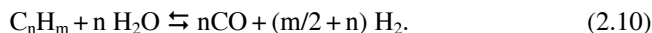
Hydrogen production from carbonaceous solid wastes requires multiple catalytic reaction steps: for the production of high-purity hydrogen, the reforming of fuels is followed by two water-gas-shift reaction steps, a final carbon monoxide purification, and carbon dioxide removal. Steam reforming, partial oxidation, and autothermal reforming of methane are well-developed processes for the production of hydrogen. Stepwise steam reforming of methane for the production of carbon-monoxide-free hydrogen has been investigated at various process conditions by Choudhary and Goodman (2000). The process consists of two steps involving the decomposition of methane to carbon-monoxide-free hydrogen and surface carbon in the first step followed by steam gasification of this surface carbon in the second step. The carbon-monoxide-free hydrogen formed in the first step is produced in the second step of the reaction. The mixture of gases can be separated and methane-rich gas mixture returned to the first step (Choudhary and Goodman, 2000). Steam, at high temperatures (975 to 1375 K), is mixed with methane gas in a reactor with a nickel-based catalyst at 3 to 25 bar pressure to yield carbon monoxide (CO) and hydrogen (H_2). Steam reforming is the process by which methane and other hydrocarbons in natural gas are converted into hydrogen and carbon monoxide by reaction with steam over a nickel catalyst on a ceramic support. The hydrogen and carbon monoxide are used as initial material for other industrial processes:



It is usually followed by the shift reaction:



The theoretical percentage of hydrogen to water is 50%. The further chemical reaction for most hydrocarbons that take place is:



It is possible to increase the efficiency to over 85% with an economic profit at higher thermal integration. There are two types of steam reformers for small-scale hydrogen production: conventional reduced-scale reformers and specially designed reformers for fuel cells.

Commercial catalysts consist essentially of nickel supported on alumina. In one study, in the conversion of cyclohexane, magnesium inhibited the formation of hydrogenolysis products. Nonetheless, the presence of calcium did not influence the metallic phase. The impregnated Ni/MgO catalyst performed better than the other types (Santos *et al.*, 2004).

Compared with other biomass thermochemical gasification processes such as air gasification or steam gasification, supercritical water gasification can directly deal with wet biomass without drying and have high gasification efficiency in lower temperatures. The cost of hydrogen production from supercritical water gasification of wet biomass is several times higher than the current price of hydrogen from steam methane reforming. In one study, biomass was gasified in supercritical water at a series of temperatures and pressures during different resident times to form a product gas composed of H_2 , CO_2 , CO , CH_4 , and a small amount of C_2H_4 and C_2H_6 (Demirbas, 2004).

The yield of hydrogen from conventional pyrolysis of corncob increases from 33 to 40% when the temperature is increased from 775 to 1025 K. The yields of hydrogen from steam gasification increase from 29% to 45% for (water/solid)=1 and from 29% to 47% for (water/solid)=2 when the temperature is increased from 975 to 1225 K (Demirbas, 2006c). The pyrolysis is carried out at moderate temperatures and steam gasification at the highest temperatures.

2.4.2 Fuels from Bio-syngas via Fischer–Tropsch Synthesis

The Fischer–Tropsch synthesis (FTS) for the production of liquid hydrocarbons from coal-based synthesis gas has been the subject of renewed interest for conversion of coal and natural gas into liquid fuels (Jin and Datye, 2000). The use of iron-based catalysts is attractive due to their high FTS activity as well as their water-gas shift reactivity, which helps make up the deficit of H_2 in the syngas from modern energy-efficient coal gasifiers (Rao *et al.*, 1992). The FTS for the production of transportation fuels and other chemicals from synthesis has attracted much attention due to the pressure from oil supplies (Dry, 1999). The interest in iron-based catalysts stems from their relatively low cost and excellent water-gas-

shift (WGS) reaction activity, which helps to make up the deficit of H_2 in the syngas from coal gasification (Wu *et al.*, 2004; Jothimurugesan *et al.*, 2000; Jun *et al.*, 2004). Hydrocarbon synthesis from biomass-derived syngas (bio-syngas) has been investigated as a potential way to use biomass. Only biomass offers the possibility to produce liquid, carbon-neutral transportation fuels (Tijmensen *et al.*, 2002). The FTS is used to produce chemicals, gasoline, and diesel fuel. The FT products are predominantly linear; hence the quality of the diesel fuel is very high. Since purified synthesis gas is used in FTS, all the products are sulfur and nitrogen free (Dry, 2002a). Given suitable economic conditions, FTS is an alternative route to liquid fuels and chemicals. Being sulfur and nitrogen free and low in aromatics, the fuels are more environmentally friendly than those produced from crude oil. In particular, the production of environmentally friendly high-quality diesel fuel is an attractive application of FTS (Dry, 1999).

Franz Fischer and Hans Tropsch first studied the conversion of syngas into larger, useful organic compounds in 1923 (Spath and Mann, 2000). Using syngas made from coal, they were able to produce liquid hydrocarbons rich in oxygenated compounds in what was termed the synthol process. Following these initial discoveries, considerable effort went into developing improved and more selective catalysts for this process. The process of converting CO and H_2 mixtures into liquid hydrocarbons over a transition-metal catalyst has become known as the Fischer–Tropsch synthesis (FTS). The first FTS plants began operation in Germany in 1938 but closed down after the Second World War. Then in 1955, Sasol, a world leader in the commercial production of liquid fuels and chemicals from coal and crude oil, started Sasol I in Sasolburg, South Africa. Following the success of Sasol I, Sasol II and Sasol III, located in Secunda, South Africa, came online in 1980 and 1982, respectively (Spath and Mann, 2000; Spath and Dayton, 2003). The FTS is an essential step in the conversion of carbon-containing feedstocks to liquid fuels such as diesel. Major advantages of the FTS are (1) its flexibility in feedstocks (natural gas, coal, biomass), (2) the large and even sustainable resources involved in the process, (3) the ultraclean (low sulfur content) products that result, and (4) its suitability for converting difficult-to-process resources. A major drawback of the FTS is the polymerizationlike nature of the process, yielding a wide product spectrum, ranging from compounds with low molecular mass like methane to products with very high molecular mass like heavy waxes.

The FTS-based gas-to-liquid (GTL) technology includes three processing steps: syngas generation, syngas conversion, and hydroprocessing. To make the GTL technology more cost effective, the focus must be on reducing both the capital and the operating costs of gas-to-liquid plants (Vosloo, 2001). For some time now the price has been up to \$60 per barrel. It has been estimated that the FT process should be viable at crude oil prices of about \$20 per barrel (Jager, 1998). The current commercial applications of the FT process are geared at the production of the valuable linear alpha olefins and of fuels such as LPG, gasoline, kerosene, and diesel. Since the FT process produces predominantly linear hydrocarbons, the production of high-quality diesel fuel is currently of considerable interest (Dry, 2004). The most expensive section of an FT complex is the production of purified

syngas, and so its composition should match the overall usage ratio of the FT reactions, which in turn depends on the product selectivity (Dry, 2002a). The industrial application of the FT process started in Germany, and by 1938 there were nine plants in operation having a combined capacity of about 660×10^3 t per year (Anderson, 1984)

According to operating conditions, FTS always produces a wide range of olefins, paraffins, and oxygenated products (alcohols, aldehydes, acids, and ketones). The variables that influence the spread of the products are temperature, feed gas composition, pressure, catalyst type, and promoters (Dry, 2002b).

The high-temperature fluidized-bed FT reactors with iron catalyst are ideal for the production of large amounts of linear olefins. As petrochemicals they sell at much higher prices than fuels. The olefin content of the C_3 , C_5 – C_{12} , and C_{13} – C_{18} cuts are typically 85, 70, and 60%, respectively (Dry, 2002b).

The Al_2O_3/SiO_2 ratio has significant influence on iron-based catalyst activity and selectivity in the process of FTS. Product selectivities also change significantly with different Al_2O_3/SiO_2 ratios. The selectivity of low-molecular-weight hydrocarbons increases and the olefin-to-paraffin ratio in the products shows a monotonic decrease with an increasing Al_2O_3/SiO_2 ratio (Jothimurugesan *et al.*, 2000). Recently, Jun *et al.* (2004) studied FTS over Al_2O_3 - and SiO_2 -supported iron-based catalysts from biomass-derived syngas. They found that Al_2O_3 as a structural promoter facilitated the better dispersion of copper and potassium and gave much higher FTS activity.

More recently, there has been some interest in the use of FTS for biomass conversion into synthetic hydrocarbons. Bio-syngas consists mainly of H_2 , CO , CO_2 , and CH_4 . Although the composition of bio-syngas is not suitable for direct use in FTS, it can be tailored by methane reforming, water-gas-shift reaction, and CO_2 removal. To maximize the utilization of carbon sources, the steam reforming of bio-syngas with additional natural gas feedstock can be considered (Bukur *et al.*, 1995; Dong and Steinberg, 1997; Specht *et al.*, 1999; Larson and Jin, 1999; Lee *et al.*, 2001). Hydrocarbon synthesis from bio-syngas has been investigated as a potential way to use biomass. FTS has been carried out using a $CO/CO_2/H_2/Ar$ (11/32/52/5 vol.%) mixture as a model for bio-syngas on coprecipitated $Fe/Cu/K$, $Fe/Cu/Si/K$, and $Fe/Cu/Al/K$ catalysts in a fixed-bed reactor. Some performances of the catalysts that depend on the syngas composition have also been presented (Jun *et al.*, 2004).

To produce bio-syngas from a biomass fuel the following procedures are necessary: (a) gasification of the fuel, (b) cleaning the product gas, (c) using the synthesis gas to produce chemicals, and (d) using the synthesis gas as an energy carrier in fuel cells. Figure 2.4 shows how liquid fuels are obtained from coal, biomass, and natural gas by FTS.

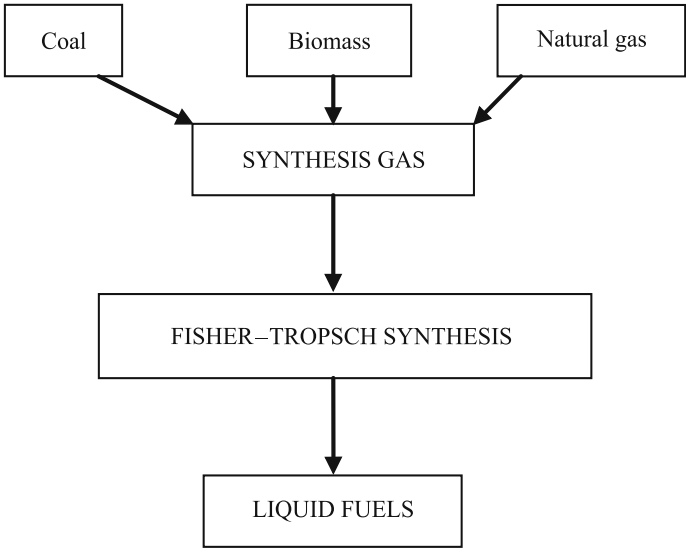


Fig. 2.4 Obtaining liquid fuels from coal, biomass, and natural gas by FTS

Figure 2.5 shows the production of diesel fuel from bio-syngas by FTS. Bio-syngas is a gas rich in CO and H₂ obtained by gasification of biomass. Biomass can be converted into bio-syngas by non-catalytic, catalytic, and steam-gasification processes.

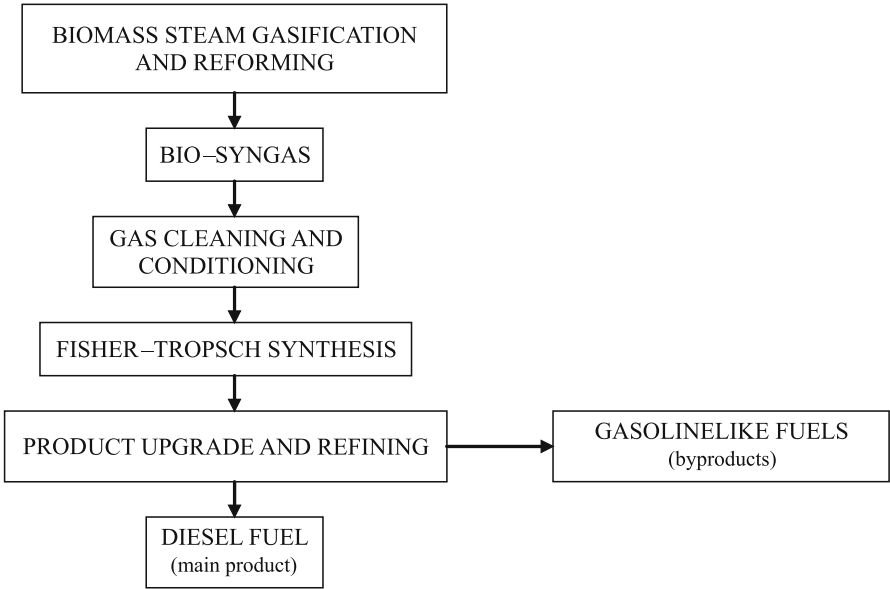
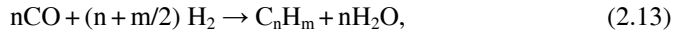
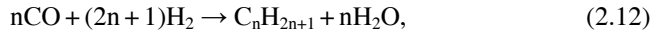
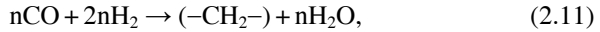


Fig. 2.5 Production of diesel fuel from bio-syngas by Fischer–Tropsch synthesis

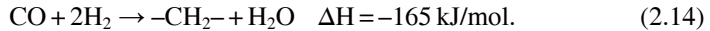
FTS was established in 1923 by German scientists Franz Fischer and Hans Tropsch. The main aim of FTS is the synthesis of long-chain hydrocarbons from a CO and H₂ gas mixture. The FTS is described by the following set of equations (Schulz, 1999; Li *et al.*, 2002):

Basic FTS reactions:

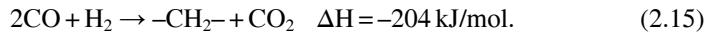


where n is the average length of the hydrocarbon chain and m is the number of hydrogen atoms per carbon. All reactions are exothermic, and the product is a mixture of different hydrocarbons in that paraffin and olefins are the main parts.

In FTS one mole of CO reacts with two moles of H₂ in the presence of a cobalt (Co)-based catalyst to yield a hydrocarbon chain extension (–CH₂–). The reaction of the synthesis is exothermic ($\Delta H = -165$ kJ/mol):



The –CH₂– is a building block for longer hydrocarbons. A main characteristic regarding the performance of FTS is the liquid selectivity of the process (Stelmachowski and Nowicki, 2003). For this reaction, given by Eq. (2.7), an H₂/CO ratio of at least 2 is necessary for the synthesis of the hydrocarbons. When iron (Fe)-based catalysts are used with water-gas-shift reaction activity, the water produced in reaction (2) can react with CO to form additional H₂. The reaction of the synthesis is exothermic ($\Delta H = -204$ kJ/mol). In this case a minimal H₂/CO ratio of 0.7 is required:



Typical operating conditions for FTS are a temperature range of 475 to 625 K and pressures of 15 to 40 bar, depending on the process. The kind and quantity of liquid product obtained is determined by the reaction temperature, pressure, and residence time, the type of reactor, and the catalyst used. Catalysts and reactors have been extensively investigated for liquid-phase FTS (Davis, 2002). Iron catalysts have a higher tolerance for sulfur, are cheaper, and produce more olefin products and alcohols. However, the lifetime of iron catalysts is short and in commercial installations generally limited to 8 weeks.

The design of a biomass gasifier integrated with a FTS reactor must be aimed at achieving a high yield of liquid hydrocarbons. For the gasifier, it is important to avoid methane formation as much as possible and convert all carbon in the biomass to mainly carbon monoxide and carbon dioxide (Prins *et al.*, 2004). Gas cleaning is an important process before FTS. Gas cleaning is even more important for the integration of a biomass gasifier and a catalytic reactor. To avoid poisoning of FTS catalysts, tar, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, alkalis, and dust particles must be removed thoroughly (Stelmachowski and Nowicki, 2003).

Synthetic FTS diesel fuels can have excellent autoignition characteristics. FTS diesel is composed of only straight-chain hydrocarbons and has no aromatics or sulfur. Reaction parameters are temperature, pressure, and H_2/CO ratio. FTS product composition is strongly influenced by catalyst composition: product from a cobalt catalyst is higher in paraffins and product from an iron catalyst is higher in olefins and oxygenates (Demirbas, 2006a).

2.5 Biodiesel

Vegetable oil (m)ethyl esters, commonly referred to as “biodiesel”, are prominent candidates as alternative diesel fuels. The name biodiesel has been given to transesterified vegetable oil to describe its use as a diesel fuel (Demirbas, 2002). There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature as opposed to conventional diesel, which is a fossil fuel that can be depleted (Ghadge and Raheman, 2006). Biodiesel is technically competitive with or offers technical advantages over conventional petroleum diesel fuel. Vegetable oils can be converted into their (m)ethyl esters via a transesterification process in the presence of a catalyst. Methyl, ethyl, 2-propyl, and butyl esters have been prepared from vegetable oils through transesterification using potassium and/or sodium alkoxides as catalysts. The purpose of the transesterification process is to lower the viscosity of the oil. Ideally, transesterification is potentially a less expensive way of transforming the large, branched molecular structure of bio-oils into smaller, straight-chain molecules of the type required in regular diesel combustion engines.

Biodiesel esters are characterized by their physical and fuel properties including density, viscosity, iodine value, acid value, cloud point, pure point, gross heat of combustion, and volatility. Biodiesel fuels produce slightly lower power and torque and consume more fuel than No. 2 diesel (D2) fuel. Biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability (Bala, 2005).

The cost of biodiesels varies depending on the base stock, geographic area, variability in crop production from season to season, the price of crude petroleum, and other factors. Biodiesel is more than twice as expensive as petroleum diesel. The high price of biodiesel is in large part due to the high price of the feedstock. However, biodiesel can be made from other feedstocks, including beef tallow, pork lard, and yellow grease (Demirbas, 2005).

Most of the biodiesel currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats such as restaurant waste and animal fats that could be converted into biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be con-

verted into biodiesel using an alkaline catalyst (Demirbas, 2003; Canakci and Van Gerpen, 2001).

Biodiesel is an environmentally friendly alternative liquid fuel that can be used in any diesel engine without modification. There has been renewed interest in the use of vegetable oils for making biodiesel due to its less polluting and renewable nature compared with conventional petroleum diesel fuel. If the biodiesel valorized efficiently at energy purpose, so would be benefit for the environment and the local population, job creation, provision of modern energy carriers to rural communities.

2.6 Bio-oil

The term bio-oil is used mainly to refer to liquid fuels. There are several reasons why bio-oils are considered relevant technologies by both developing and industrialized countries. They include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector.

Bio-oils are liquid or gaseous fuels made from biomass materials such as agricultural crops, municipal wastes, and agricultural and forestry byproducts via biochemical or thermochemical processes. They can replace conventional fuels in vehicle engines, either totally or partially in a blend (EC, 2004). The organic fraction of almost any form of biomass, including sewage sludge, animal waste, and industrial effluents, can be broken down through anaerobic digestion into a methane and carbon dioxide mixture called “biogas”. Biogas is an environment friendly, clean, cheap, and versatile fuel (Kapdi *et al.*, 2005).

Pyrolysis/cracking is defined as the cleavage to smaller molecules by thermal energy. Hydrogen can be produced economically from woody biomass (Encinar *et al.*, 1998). Biomass can be thermally processed through gasification or pyrolysis to produce hydrogen. The main gaseous products from biomass are the following (Wang *et al.*, 1997):

Pyrolysis of biomass $\rightarrow \text{H}_2 + \text{CO}_2 + \text{CO} + \text{Gaseous and liquid hydrocarbons}$, (2.16)

Catalytic steam reforming of biomass $\rightarrow \text{H}_2 + \text{CO}_2 + \text{CO}$, (2.17)

FT synthesis of $(\text{H}_2 + \text{CO}) \rightarrow \text{Gaseous and liquid hydrocarbons}$. (2.18)

If the purpose were to maximize the yield of liquid products resulting from biomass pyrolysis, a low temperature, high heating rate, short gas residence time process would be required. For a high char production, a low temperature, low heating rate process would be chosen (Bridgwater, 2003). If the purpose were to maximize the yield of fuel gas resulting from pyrolysis, a high temperature, low heating rate, long gas residence time process would be preferred (Encinar *et al.*, 1998).

Fischer–Tropsch liquids from natural gas and ethanol from biomass may become widespread. The Fischer–Tropsch liquids will compete with petroleum if

natural gas is imported at very low prices and the sulfur content of the liquids is much lower than that of petroleum diesel fuel (MacLean and Lave, 2003). Figure 2.6 shows the production facilities of green diesel and green gasoline and other fuels from bio-syngas by FTS.

FTS can be carried out in a supercritical fluid medium (SFM). When hexane is used as the fluid, with increasing pressure in the supercritical medium, the density and heat capacity of the hexane-dominated phase increase. The decrease in mass transfer rates at the higher pressure is offset somewhat by the increase in the intrinsic reaction rates. At a space velocity of 135 g hexane/g catalyst/h, end of run (8 h) isomerizations are roughly twofold higher and deactivation rates are three-fold lower in near-critical reaction mixtures when compared to subcritical reaction mixtures (Balat, 2006).

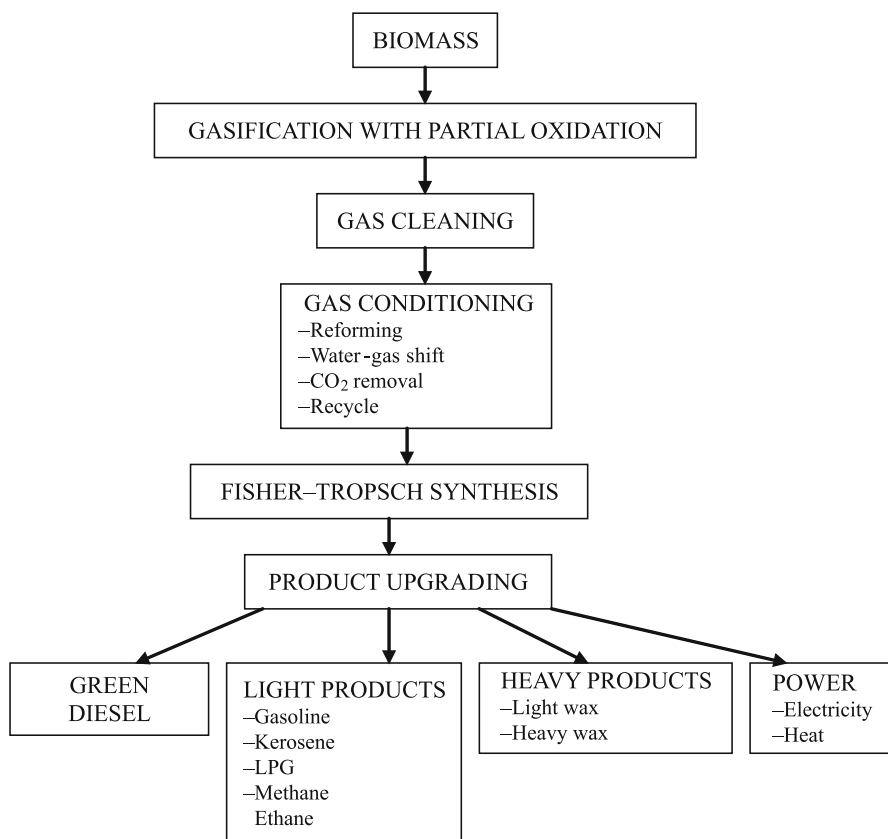


Fig. 2.6 Green diesel and green gasoline facilities from biomass via Fischer-Tropsch synthesis

2.7 Global Biofuel Scenarios

Renewable resources are more evenly distributed than fossil and nuclear resources, and energy flows from renewable resources are more than three orders of magnitude higher than current global energy use. Today's energy system is unsustainable because of uncompetitive issues as well as environmental, economic, and geopolitical concerns that have implications far into the future (UNDP, 2000).

According to the International Energy Agency (IEA), scenarios developed for the USA and the EU indicate that near-term targets of up to 6% displacement of petroleum fuels with biofuels appear feasible using conventional biofuels, given available cropland. A 5% displacement of gasoline in the EU would require about 5% of available cropland to produce ethanol, while in the USA 8% would be required. A 5% displacement of diesel would require 13% of US cropland and 15% in the EU. The recent commitment by the US government to increase bioenergy threefold in 10 years has added impetus to the search for viable biofuels (IEA, 2004).

Dwindling fossil fuel stocks and the increasing dependency of the USA on imported crude oil have led to a major interest in expanding the use of bioenergy. The EU has also adopted a proposal for a directive promoting the use of biofuels with measures ensuring that biofuels would account for at least 2% of the market for gasoline and diesel sold as transport fuel by the end of 2005, increasing in stages to a minimum of 5.75% by the end of 2010 (Hansen *et al.*, 2005). Biomass can be converted into biofuels such as bioethanol and biodiesel and thermochemical conversion products such as syn-oil, bio-syngas, and biochemicals. Bioethanol is a fuel derived from renewable sources of feedstock, typically plants such as wheat, sugar beet, corn, straw, and wood. Bioethanol is a petroleum additive/substitute, and biodiesel is better than diesel fuel in terms of sulfur content, flash point, aromatic content, and biodegradability (Bala, 2005).

Figure 2.7 shows the alternative fuel projections for total automotive fuel consumption in the world. Hydrogen is currently more expensive than conventional energy sources. There are different technologies presently being applied to produce hydrogen economically from biomass. Biohydrogen technology will play a major role in the future because it can utilize renewable sources of energy (Nath and Das, 2003).

Hydrogen for fleet vehicles will probably dominate in the transportation sector in the future. To produce hydrogen via electrolysis and the transportation of liquefied hydrogen to rural areas with pipelines would be expensive. The production technology would be site specific and include steam reforming of methane and electrolysis in hydropower-rich countries. In the long run, when hydrogen is a very common energy carrier, distribution via pipeline is probably the preferred option. The cost of hydrogen distribution and refueling is very site specific.

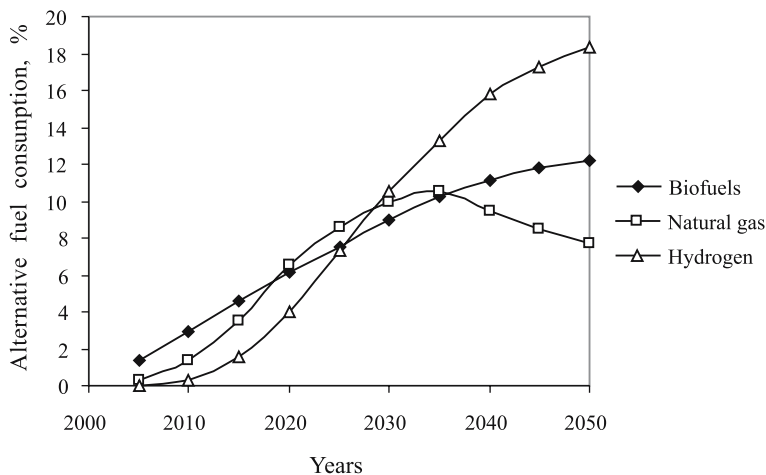


Fig. 2.7 Alternative fuel projections for total automotive fuel consumption in the world
Source: Demirbas, 2006a

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